



Synthesis, Characterization and Photo-Electrochemical Conversion of 3, 5-Diamino-4-[(E)-(6-Hydroxy-1, 3-Benzothiazol-2-Yl)Diazenyl]-2-(Tricyanoethenyl) Benzoic Acid

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ABSTRACT

Recently, the organic materials have gained considerable attention in photovoltaic and optoelectronic applications such as batteries, organic field-effect transistors and organic photovoltaic cells. This work is centered on synthesis, characterization and photo-electrochemical conversion of 3, 5-diamino-4-[(e)-(6-hydroxy-1, 3-benzothiazol-2-yl)diazenyl]-2-(tricyanoethenyl) benzoic acid. Standard procedures were used to successfully synthesize two novel dyes with the structural configuration of D- π -bridge-D-A (donor- π -bridge-donor-acceptor). The colour of the dye spans from brown red to dark brown with a melting point that spans from 164-182°C. The ¹H and ¹³C-NMR spectroscopy for dye 44 and 66 and from the result seven signals with a highly characteristic de-shielded carboxylic protons at 10.40 ppm (¹H, Singlet) and the hydroxyl protons 10.04 ppm. The ¹³C -NMR spectrum of the Dye 44 showed a signal at 173.51 ppm for carbon atom of the carboxylic groups while a signal at 157.29 ppm was attributable to the carbon atom of the thiazole ring. The ability of a solar cell to generate photocurrent at a given wavelength of the incident light was measured by the incident monochromatic photon to current conversion efficiency (IPCE) and the result was observed to ranged from 54.9% (at 440 nm) and 54% (at 420nm) for Dye 66 which confirm that photon from sun have been fully converted into current.

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INTRODUCTION

Dye sensitized solar cells (DSSCs), a third-generation solar cell discovered in early 1990s, have gained intensive attention and been considered as promising alternative for fossil fuel energy (Shoji *et al.*, 2009). DSSCs offer advantages over the conventional silicon based solar cell due to cost effectiveness, flexibility in shape, easy accessibility of dye resources, and noteworthy performance (Zhang and Cao, 2011). The dye sensitized solar cell (DSSC) is a photo-

electrochemical device that is inspired to the photosynthesis process, where a dye is used to catch the light then transformed into electricity. (Grätzel, 2004). Sensitizer in the cell absorbs photons and induces excitation of electron to the wide band-gap semiconductor, dyes, and electrolytes. The device is comprised of two faced electrodes, a photoanode and a counter electrode, with an electrolyte in between. (Elena, 2011).

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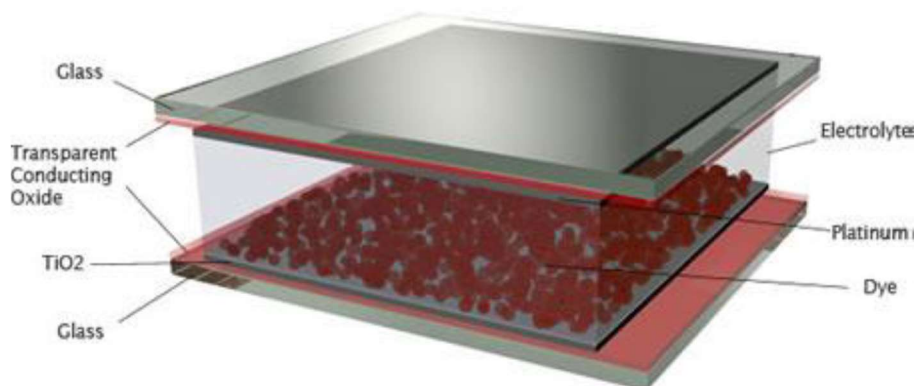
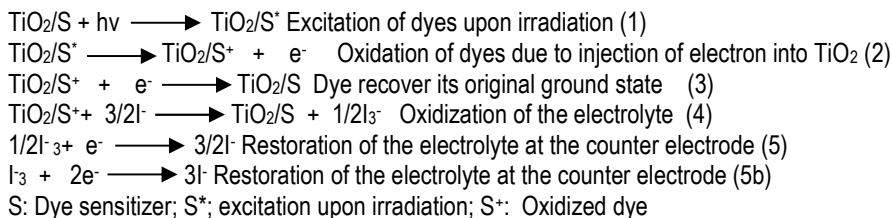


Figure 1: Schematic overview of the dye sensitized solar cell (DSSC) (Kuo *et al.*, 2010)

Figure 1 shows the schematic overview of the dye sensitized solar cell. Here both electrodes are usually made from a sheet of common floating glass coated on one side with a thin transparent conductive layer of fluorine-doped tin dioxide (FTO) or indium-doped tin oxide (ITO). The cathode is a conductive glass covered with a few clusters of metallic platinum which has a catalytic effect in the reduction process of the electronic mediator acceptor member. In the photoanode, the transparent conductive electrode is covered with a thin film of a mesoporous semiconductor oxide, normally TiO₂ (anatase) although alternative wide band gap oxides such as ZnO and Nb₂O₅ have also been investigated. Attached to the surface of the nanocrystalline film is a monolayer of the charge transfer dye (S). Photo-excitation of the sensitizer (S*) results in the injection of an electron into the conduction band of the oxide. The original state

of the dye (S) is subsequently restored by electron donation from the electrolyte, usually an organic solvent containing redox system, such as the iodide/triiodide (I/I₃) couple. The regeneration of the sensitizer by iodide intercepts the capture of the conduction band electron by the oxidized dye. The iodide is regenerated in turn by the reduction of triiodide at the counter electrode and the circuit being completed via electron migration through the external load. A schematic presentation of the operating principles of the fundamental requirement for the well-working of the process are that the excited state of the sensitizer must be higher in energy in respect of the bottom of the semiconductor's conduction band while the dye's oxidized state must be lower in energy of the potential of the redox system. (Ecole Polytechnique Federale de Lausanne, 2008). The transfer of electron during cell operation involves the following steps:



The entire cycle consists in the quantum conversion of photons to electrons as a

result, no net chemistry occurs, but electrical work has been produced.

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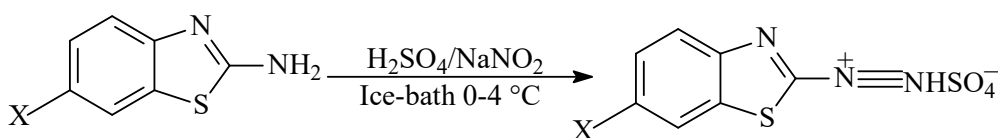
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MATERIALS AND METHODS

Materials

Analytical grade reagents and chemicals from Sigma Aldrich were used for this research work. These include; tetracyanoethylene, 4-hydroxyaniline, ammoniumthiocyanates, 3-amino-2-methylbenzoic acid, sodium nitrite, Magnetic stirrer, oven, reflux condenser, melting point apparatus, Uv-visible spectrophotometer,

Methods



2-aminobenzothiazole

diazonium salt of 2-aminobenzothiazole

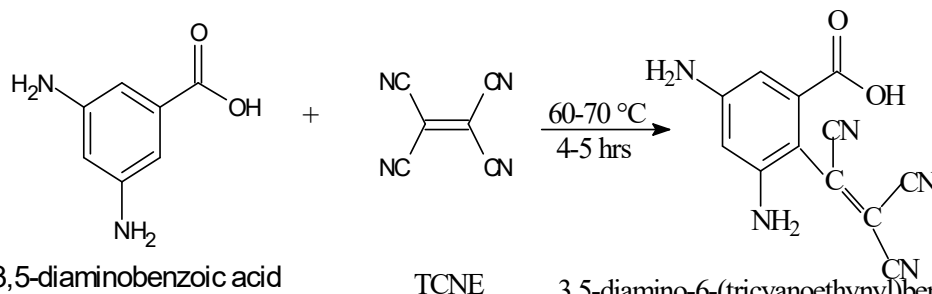
Scheme 2: Diazotization of 2-aminobenzothiazole

Where X is OH and CH₃

Tricyanovinylating of the 3, 5-Diaminobenzoic acid

A solution of the requisite benzoic acid derivative (0.01 mol, 3 g) and (0.01 mol, 0.8 g) tetracyanoethylene (TCNE) in DMF (20 ml) was

stirred at 60- 90 °C for 5-7 hr. The solvent was removed and the residual solid was collected and re-crystallized from toluene/chloroform mixture Abdullah *et al.*, (2015). As shown in the reactions below:



3,5-diaminobenzoic acid

TCNE

3,5-diamino-6-(tricyanoethynyl)benzoic acid

Scheme 3: Tricyanovinylating of 3, 5-diaminobenzoic acid

Coupling Reaction

Separately, the coupling components hydrazones derivative were dissolved in DMF and cooled to 0°C by adding ice. The intermediate from 2-aminobenzothiazole diazonium solutions were then added separately for 30-40 minutes with vigorous stirring (Maradiya and Patel, 2010). The mixture was agitated for another 3 hours at 5°C before the pH of the

solution was adjusted to 4-5 with 5 ml of 10% NaOH. The finished product was filtered, rinsed, and dried. The crude product was refined by re-crystallizing it from a 9:1 mixture of ethanol and DMF.

Characterization of the synthesized dyes.

The physicochemical properties of synthesized dyes and the azo dyes were carried out and spectroscopic properties such as Uv-

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visible spectroscopy, FT-IR, GC-MS and ^1H and ^{13}C -NMR spectroscopy.

Photo-Electrochemical Measurement of Incident Photon to Current Conversion Efficiency

The incident light intensity was calibrated using a reference Si solar cell (Newport Oriel.91150 V) to set 1 Sun (100

mW/cm^2). Incident monochromatic photon to current conversion efficiency measurement was fully controlled under (Newport 2636-R) IPCE measurement system equipped with a 75 W short arc Xenon lamp as the light source connected to a monochromator. Calibration of the incident light was performed before measurements using a silicon photo-diode.

RESULT AND DISCUSSION

Table 1a: Structures with IUPAC Names of the Dyes for DSSCs

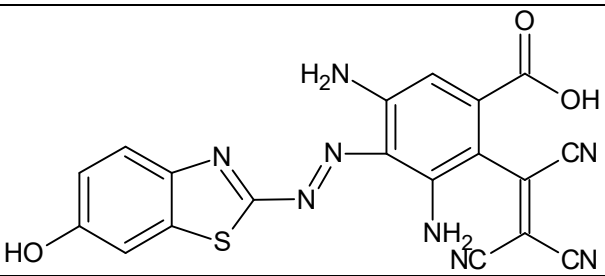
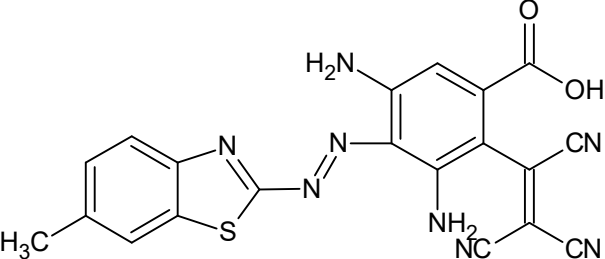
Dye no	IUPAC Names	Structures of the Synthesized Dyes
DYE 44	3,5-diamino-4-[(E)-(6-hydroxy-1,3-benzothiazol-2-yl)diazenyl]-2-(tricyanoethyl) benzoic acid	
DYE 66	3,5-diamino-4-[(E)-(6-methyl-1,3-benzothiazol-2-yl)diazenyl]-2-(tricyanoethyl)benzoic acid	

Table 1b: Physical Properties of the Synthesized Dyes

Dye No	Molecular formula	Theoretical Molecular Weight (g/mol)	Melting Point ($^{\circ}\text{C}$)	Yield %	Physical appearance
Dye 44	$\text{C}_{19}\text{H}_{10}\text{N}_8\text{O}_3\text{S}$	430.4	164-166	85	Brown red
Dye 66	$\text{C}_{20}\text{H}_{12}\text{N}_8\text{O}_2\text{S}$	428.4	181-182	73	Dark brown

The physical characteristics of the synthesized compounds are shown in Table 1b. The color of the dye are brown red and dark brown which can be linked to variations in the substituent group such as OH and CH_3 found in

diazo compounds 2-aminobenzothiazole. The melting point of the dye ranged from 164-182 $^{\circ}\text{C}$ and the closeness in range is an indication of a pure compound. (Wong *et al.*, 2002).

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Table 2.0: UV-visible Spectroscopic data of the synthesized dyes in ethanol and dimethylsulfoxide (DMSO)
Solvent λ_{max} (nm)

Dye no	Ethanol	DMSO
DYE 44	463	560
DYE 66	429	576

Heterocyclic based azo dyes tends to show large solvatochromic effects than azo benzene based dyes because of increase polarity of the dye system, especially in excited state. According to Zollinger (1991), bathochromic shifts are found with increasing

solvent polarity when the excited is more polar than the ground state as shown in Table 2.0 with dye 66 having the wavelength of maximum absorption in DMSO, where as hypsochromic shift was observed in ethanol.

Table 3.0: FT-IR Vibrational Frequencies of the Synthesized Dyes

Dye	FT-IR Vmax (cm ⁻¹)
Dye 44	3328.5 (OH, N-H str.), 2221.5 (CN str.), 1602.8, 1662.4 (C=N), 1528.2 (N=N str.), 752.9 (C-S)
Dye 66	3354.6, 3313.6, 3194.3 (N-H, OH str.), 2918.5, 2851.4 (C-H str.), 2206.6 (CN str.), 1651.2 (C=N str.), 1599.0, 1520.8 (N=N), 745.5 (C-S)

Table 4.0: GC-MS spectroscopy of the Synthesized Dyes

Dye no	Molecular formula	Experimental values of m/z fragment	Corresponding positive charge fragment	Theoretical value
Dye 44	C ₁₉ H ₁₀ N ₈ O ₃ S	55.1, 95.1, 135.1, 163, 253.8, 203.2, 430.0	C ₂ H ₃ N ₂ ⁺ , C ₆ H ₆ O ⁺ , C ₆ H ₂ NSO ⁺ , C ₇ H ₃ N ₂ SO ⁺ , C ₁₃ H ₇ N ₃ SO ⁺ , C ₈ H ₂ N ₃ SO ₂ ⁺ , M	430.4
Dye 66		55.1, 139.1, 111.0, 222.2, 264.3, 429.3	C ₂ H ₃ N ₂ ⁺ , C ₆ H ₅ NSO ⁺ , C ₃ N ₃ S ⁺ , C ₁₂ H ₄ N ₃ O ₂ ⁺ , C ₁₄ H ₈ N ₄ S ⁺ , M	428.4

The mass spectroscopy for dye 44 and 66 revealed fragmentation pattern of C₂H₃N₂⁺, C₆H₆O⁺, C₆H₂NSO⁺, C₇H₃N₂SO⁺, C₁₃H₇N₃SO⁺, C₈H₂N₃SO₂⁺ and C₂H₃N₂⁺, C₆H₅NSO⁺, C₃N₃S⁺,

C₁₂H₄N₃O₂⁺, C₁₄H₈N₄S⁺ the molecular ion (M⁺) at m/z 430.0 and 429.3 g/mol which is in agreement with the theoretical molecular weight of 430.4 and 429.3 g/mol for dye 44 and 66.

Table 5.0: ¹H and ¹³C-NMR (400 MHz, DMSO): δ H(ppm) Data of the Synthesized Dyes

Dye	¹ H and ¹³ C-NMR
Dye 44	¹ H: 10.40(S,1H,COOH), 10.04(S, 1H, OH), 8.32(d,1H, J=12 Hz), 8.26(d, 1H, J=12 Hz), 8.14(S, 4H, 2NH ₂), 7.86(S, 1H), 7.60(S, 1H); ¹³ C-NMR(400 MHz, DMSO-d ₆): δ (ppm) 173.51, 157.29, 148.18, 145.95, 142.76, 141.74, 140.47, 139.69, 138.32, 136.69, 136.42, 132.58, 130.53,

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Dye 66

129.20, 128.75, 126.88, 122.46, 119.73
10.39(S, 1H, COOH), 8.11(S, 4H, 2NH₂), 7.93(S, 1H),
7.8(d, 1H, J=8.0 Hz), 7.73(S, 1H), 6.85(d, 1H,
J=12.0Hz), 1.89(S, 3H, CH₃);
¹³C- NMR(400 MHz, DMSO-d₆):δ(ppm) 169.49,
158.86, 157.17, 156.26, 156.07, 145.45, 144.18,
140.69, 138.96, 137.39, 133.49, 130.82, 128.94,
128.23, 125.94, 125.19, 121.26, 114.59, 18.02

Table 4.0 showed the ¹H and ¹³C-NMR spectroscopy for dye 44 and 66 and from the result seven signals with a highly characteristic de-shielded carboxylic protons at 10.40 ppm (1H, Singlet) and the hydroxyl protons 10.04 ppm. Also 8.14 ppm was observed due to the presence of amino protons which are also within the same chemical environment, two signals were observed for pairs of aromatic protons in

the 8.26 – 8.32 ppm range with a coupling constant of 12 Hz. The ¹³C –NMR spectrum of the Dye 44 showed a signal at 173.51 ppm for carbon atom of the carboxylic groups while a signal at 157.29 ppm was attributable to the carbon atom of the thiazole ring. The signal at 148.18 – 119.73 ppm were observed for aromatic carbon.

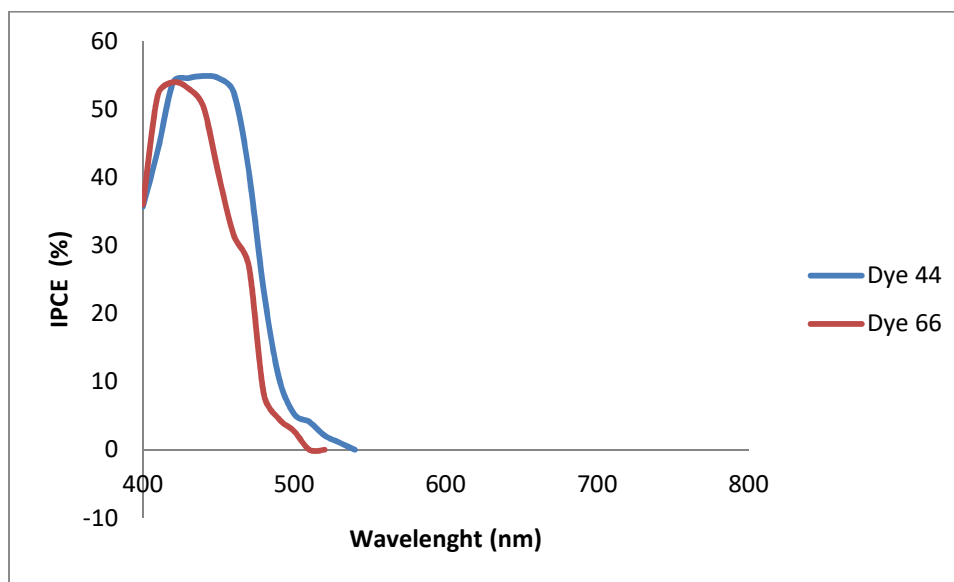


Figure 2.0: Incident photon to current conversion efficiency (IPCE) of the photo-sensitizers

The photocurrent collected at different wavelength, relative to the number of photons incident on the surface at that wavelength determine the spectra response of the device sometimes known as the external quantum efficiency or best known as incidence photon to current conversion efficiency or collection

efficiency at each wavelength. Light of different wavelength is absorbed at different depth in TiO₂/dye photoanode film. The ability of a solar cell to generate photocurrent at a given wavelength of the incident light was measured by the incident monochromatic photon to current conversion efficiency (IPCE), define as the

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number of electron generated by number of incident photons (Tomar *et al.*, 2020).

$$IPCE = \frac{1240 \times J_{SC}}{\lambda \times P_{in}}$$

J_{sc} is the short circuit photocurrent density for monochromatic irradiation, and λ and P_{in} the wavelength and the intensity respectively of the monochromatic light.

The IPCE spectra of the different TiO₂-based DSSCs are displayed in figure 2.0 as highlighted in Table 4.0, the highest value of IPCE is 54.9% (at 440 nm) and 54% (at 420nm) for Dye 66. Thus IPCE correlates often to the absorption spectrum of the active layer but a strong deviation cannot often be excluded (Wu *et al.*, 2010). It is imperative to stress that all the devices are identical in all respect but for the dye molecules, so difference in IPCE can be reasonably attributed to different dye molecular properties (Gurpreet *et al.*, 2016).

CONCLUSION

Two azo dyes were synthesized, purified and characterized via analytical techniques such UV-visible spectroscopy, FT-IR spectroscopy, GC-MS and ¹H and ¹³C-NMR spectroscopy. The colour of the dyes ranges from brown red to dark brown with an impressive yield. The solvatochromic effect of the dyes was carried out in ethanol and DMSO. The FT-IR spectroscopy studied of all the dyes showed various absorption bands. The GC-MS studies of all the dyes have a molecular ions that spans from 428.8-430 consistent with the theoretical molecular weight of the dyes. Also the H-NMR of all the dyes confirm a highly de-shielded signals that spans from 10.39-10.40 ppm attributable to the OH of the carboxylic groups. The incident monochromatic photon to current conversion efficiency (IPCE) was observed to range from 54.9% (at 440 nm) and 4% (at 420nm) for Dye 66.

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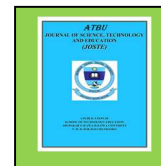
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